

# Grape extract assisted green synthesis of reduced graphene oxide for water treatment application

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## Abstract

Grapes (*Vitis Vinifera*) extract was explored as a “green reducing agent” for the preparation of reduced graphene oxide (RGO) from graphene oxide (GO). The effect of reduction time on physical, chemical and optical properties of the RGO was also investigated. Synthesized RGO samples exhibited excellent activity as an adsorbent for the removal of organic dye. Proposed synthesis is environmental friendly, cost effective and seems promising for the large scale production of RGO.

**Keywords:** Carbon materials, X-ray techniques, green synthesis, reduced graphene oxide, grapes extract

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## 1. Introduction

Graphene, owing to its exotic physical and electrical properties has led the recent advances in material sciences and is finding its way into various fields including electronics, biomedical, environment and engineering [1]. Chemical reduction of graphene oxide (GO) is one of the highly explored synthesis approaches for the graphene preparation. The synthesis approach involves oxidation of graphite via Hummers method followed by chemical reduction using harsh chemical reducing agents e.g., hydrazine [2] and  $\text{NaBH}_4$  [3]. The involvement of hazardous chemical reducing agents in the second step is a major drawback and ongoing efforts are there to find environment friendly and safe green reducing agents. Environmentally benign reducing agents such as ascorbic acid [4], sugar [5], amino acids [6] and plant extracts [7, 8] have recently been utilized for the reduction of GO to reduced graphene oxide (RGO). Plant extracts are attractive alternatives to the toxic chemical reducing agents as these are easily available, comparatively cheap and environmental friendly.

Grapes (*Vitis vinifera*) extract is a rich source of phytochemicals e.g., polyphenols, flavonoids and catechins, which are capable of reducing gold and silver salts to their metallic form [9]. Apart from preparation of metal nanoparticles, grapes extract has also shown remarkable performance as a reducing agent for the selective reduction of ketone [10] and nitro compounds [11]. These reports confirm that grapes extract holds immense potential as a reducing agent. The phytochemicals present in the grapes extract are of great medicinal value and also environmentally benign, which makes these an attractive alternative to the conventional toxic reducing agents.

## 2. Experimental

Graphite LR was procured from Alfa Aesar. Fresh grapes were purchased from local market. De-ionized water was used in the preparation of all the solutions.

Graphene oxide was prepared using modified Hummers method [12-14]. Typically, 1 gm of graphite and 23 ml of concentrated  $\text{H}_2\text{SO}_4$  were taken in a conical flask and the reaction mixture was placed on an ice bath. About 3 g of  $\text{KMnO}_4$  was slowly added to the reaction mixture under constant stirring at temperatures of  $0-5^\circ\text{C}$  and was further stirred for another 30 minutes. The flask was then transferred on a hot plate with a preset temperature of

35°C, and kept for 1 hour. After completion of heating period, 46 ml of de-ionized water was added to the reaction mixture followed by vigorous stirring. As obtained reaction mixture was then further heated on a boiling water bath for 30 minutes. 10 ml of 30% H<sub>2</sub>O<sub>2</sub> was added to the reaction mixture to stop the reaction, followed by addition of 140 ml of de-ionized water. Yellow colour graphene oxide was obtained which was filtered and washed repeatedly using 10% HCl followed by de-ionized water and ethanol.

40 gm grapes were crushed and transferred in to a round bottom flask containing 100 ml de-ionized water. As prepared reaction mixture was heated up to boiling and allowed to boil for 10 minutes. After completion of heating the reaction mixture was allowed to cool down to room temperature and filtered to obtain a red colour extract. 30 mg GO was added to the 50 ml extract and stirred vigorously in order to disperse the GO uniformly throughout the extract. 180 µl aqueous NH<sub>3</sub> solution was added to the above reaction mixture, which changed the colour of it from red to dark green. Reaction mixture was placed on an oil bath and heated at 95°C for different time intervals (1, 3 and 6 hours) with a water condenser to avoid the evaporation of water. After completion of heating periods, the RGO samples were filtered, washed and dried in an air oven at 70°C.

UV-Vis spectra aqueous dispersion of GO and RGO samples were recorded using UV-Vis spectroscopy (Thermo Scientific Evolution 201). X-ray analysis was performed using Rigaku miniflux X-ray diffractometer (XRD). Morphology and structure of RGO was investigated using transmission electron microscope (TEM, TECNAI G<sup>2</sup>20 S-TWIN).

20 mg RGO-6hrs was added to the 100 ml malachite green solution (5 ppm). A fixed volume of the dye solution was taken out after regular time intervals and centrifuged for the removal of RGO. Absorbance for all extracted dye samples was recorded at 617 nm. Removal percentage was estimated by using the following formula [15].

$$\text{Removal percentage} = (A_0 - A_t) / A_0 \times 100 \quad (1)$$

Where A<sub>0</sub> is the initial absorbance of dye and A<sub>t</sub> is absorbance after a time interval 't'. The adsorption amount q<sub>t</sub> was calculated using following equation [16]:

$$q_t = [(C_0 - C_t) V] / m \quad (2)$$

Where  $q_t$  is the amount of adsorbed dye per gram of the adsorbent (mg/g),  $C_0$  and  $C_t$  are the concentrations of the MG solution (mg/L) at the initial and adsorption time  $t$ , respectively.  $V$  is the volume of the MG solution (L) and  $m$  is the mass of the adsorbent (g) used.

### 3. Results and discussion

The UV-Vis spectrum of GO (Fig. 1a) exhibits a peak at 230 nm and a shoulder peak at 300 nm. The peak at 230 nm can be corresponded to  $\pi$ - $\pi^*$  transitions of aromatic C=C, while the shoulder peak originates from  $n$ - $\pi^*$  transition of the C=O bonds [17]. The absorption spectra of RGO samples (Fig. 1b) exhibit a single peak around 270 nm. This red shift in the absorption spectrum from 230 to 270 nm points towards the restoration of  $sp^2$  hybridized carbon network due to removal of the oxygen bearing functional groups. An increase in the absorbance around 600 nm on increasing the reduction time from 1 to 6hrs has also been observed (Fig. 1b).

The FTIR spectrum of GO (Fig.1c) comprises of a broad peak at  $3180\text{ cm}^{-1}$  and a sharp peak at  $1615\text{ cm}^{-1}$ , which can be ascribed to stretching and deformation vibrations, respectively of physically adsorbed water. Peaks at  $1715$ ,  $1360$  and  $1040\text{ cm}^{-1}$  can be corresponded to C=O,  $\text{COO}^-$  and C-O stretching vibrations, respectively. However, with the increase in the reduction time the intensity of these peaks reduced significantly and after 6 hrs of reaction time, most of the peaks assigned to oxygen containing groups almost disappeared (Fig.1c), confirming the efficient reduction of GO by the grapes extract.

The XRD-diffraction pattern of graphite exhibits one sharp basal reflection peak at  $2\theta$  value of  $26^\circ$  (d-spacing of 0.357 nm) corresponding to (002) plane (Fig. 2a). Oxidation of graphite to graphene oxide results in a shift in this peak towards lower  $2\theta$  value  $10.4^\circ$  (d-spacing 0.850 nm). This large increase in the d-spacing indicates the intercalation of water molecules as well as formation of oxygen containing functional groups in between the graphite layers. In the case of RGO-6hrs sample, the sharp peak at  $10.4^\circ$  disappeared, however, a broad peak at approximately similar  $2\theta$  value can still be observed suggesting the presence of residual oxygen functionalities in the sample. Simultaneously, a new ~~another new~~ broad peak, centred at  $23.7^\circ$ , was also observed ~~can also be seen indicative of the formation of few layered graphene structure indicating formation of few layers of graphene~~ [18, 19]. The transmission electron microscopy TEM image of RGO-6hrs sample shows that the sample consists of aggregated and wrinkled few layers of graphene. These

wrinkles and corrugations endow thermodynamic stability to the two-dimensional graphene sheets.

For dye absorption experiments, 20 mg RGO was utilized to treat 100 ml malachite green solution (5 ppm). A sharp decrease in the absorbance for the initial 5 minutes indicates that most of the dye was removed in first 5 minutes (Fig. 3). Graph plotted between removal percentage and time (Fig. 3 inset) shows that for all the samples (GO, RGO-1hr, RGO-3hrs and RGO-6hrs) most of the dye has been removed in first 10 minutes, -after which the wards adsorption process achieved equilibrium. The order of removal percentage in the first 10 minutes for all the samples was found to be following:

$$\text{GO} < \text{RGO-6hrs} < \text{RGO-1hr} \sim \text{RGO-3hrs}$$

The removal percentage of the GO was found to be lowest as compared to compare to the RGO-1hr, RGO-3hrs and RGO-6hrs samples. We believe that ~~The~~ reason behind the lowest removal percentage for the GO might be the presence of trace amount of GO which leftover in the dye solution after centrifugation.

Pseudo second order kinetic was applied in order to analyze the kinetic data, which can be defined using following equation:

$$t/q_t = 1/(K_2 q_e^2) + t/q_e \quad (3) [16]$$

Where  $q_t$  and  $q_e$  are the amounts of adsorbed malachite green on the adsorbent (g/mg) at time  $t$  and at equilibrium respectively, and  $K_2$  is the pseudo-second order rate constant ( $\text{gmg}^{-1}\text{min}^{-1}$ ). Fig.S2 shows the graph between  $q_t$  and time, it can be seen from the graph that in the initial 5 minutes adsorption is fast and afterward the rate of the adsorption has been reduced and achieved equilibrium. Fig.S3 depicts graph showing values of the  $t/q_t$  plotted as a function of time. The value of correlation coefficient ( $R^2$ ) is around 0.999 for all the samples suggesting suitability of second order kinetics model for explaining adsorption kinetics of MG dye on GO and RGO samples.

#### 4. Conclusions

An environmental benign, economical and facile synthesis approach for the preparation of reduced graphene oxide has been demonstrated. Aqueous extract of grapes (*Vitis Vinifera*) has been successfully utilized for the reduction of GO. An increase in the reduction time increased the extent of reduction also. Owing to the ease of availability of grapes worldwide, the developed synthesis methodology can be adopted for the large scale production of RGO.

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## Figure captions

Figure 1 (a) UV-Vis spectrum of GO and real pictures of GO and RGO aqueous suspension (Inset) (b) UV-Vis spectra of RGO samples (c) FTIR spectra of GO and RGO samples.

Figure 2 (a) XRD of Graphite, GO and RGO-6hrs (b) TEM image of RGO-6hrs sample

Figure 3 Removal of Malachite green dye using RGO-6hrs sample and graph showing change in the removal percentage with time for GO, RGO-1hr, RGO-3hrs and RGO-6hrs samples (Inset)

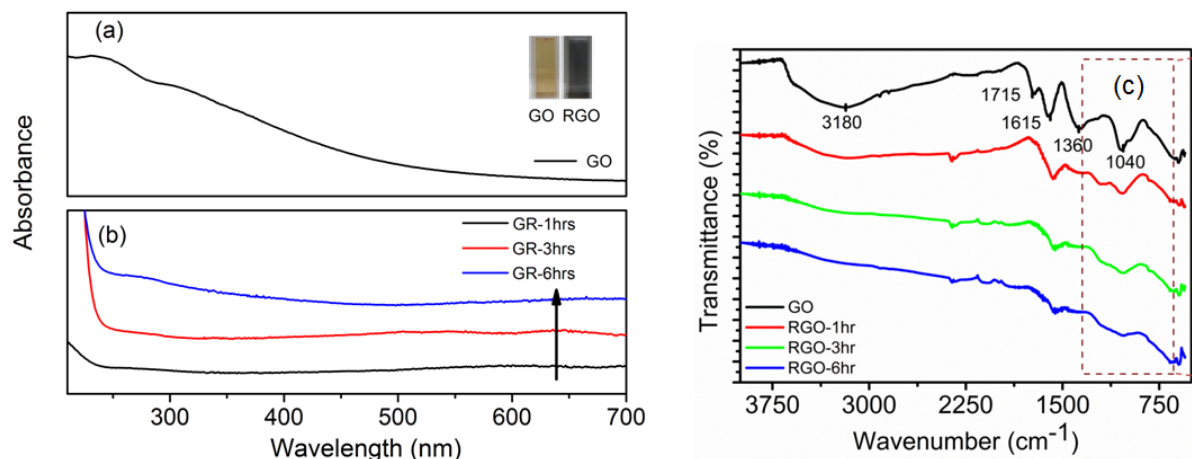


Figure 3 (a) UV-Vis spectrum of GO and real pictures of GO and RGO aqueous suspension (Inset) (b) UV-Vis spectra of RGO samples (c) FTIR spectra of GO and RGO samples.



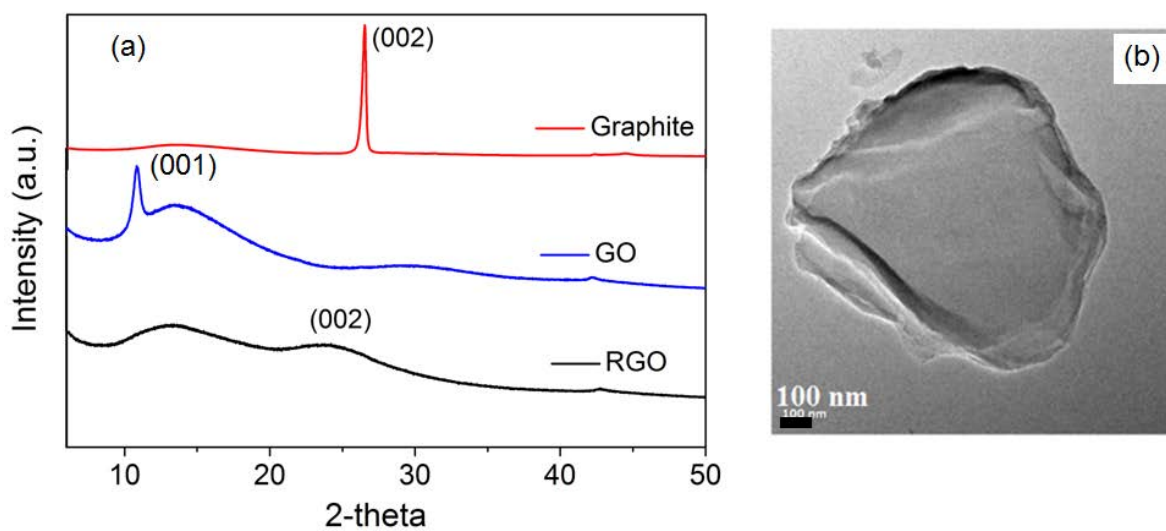
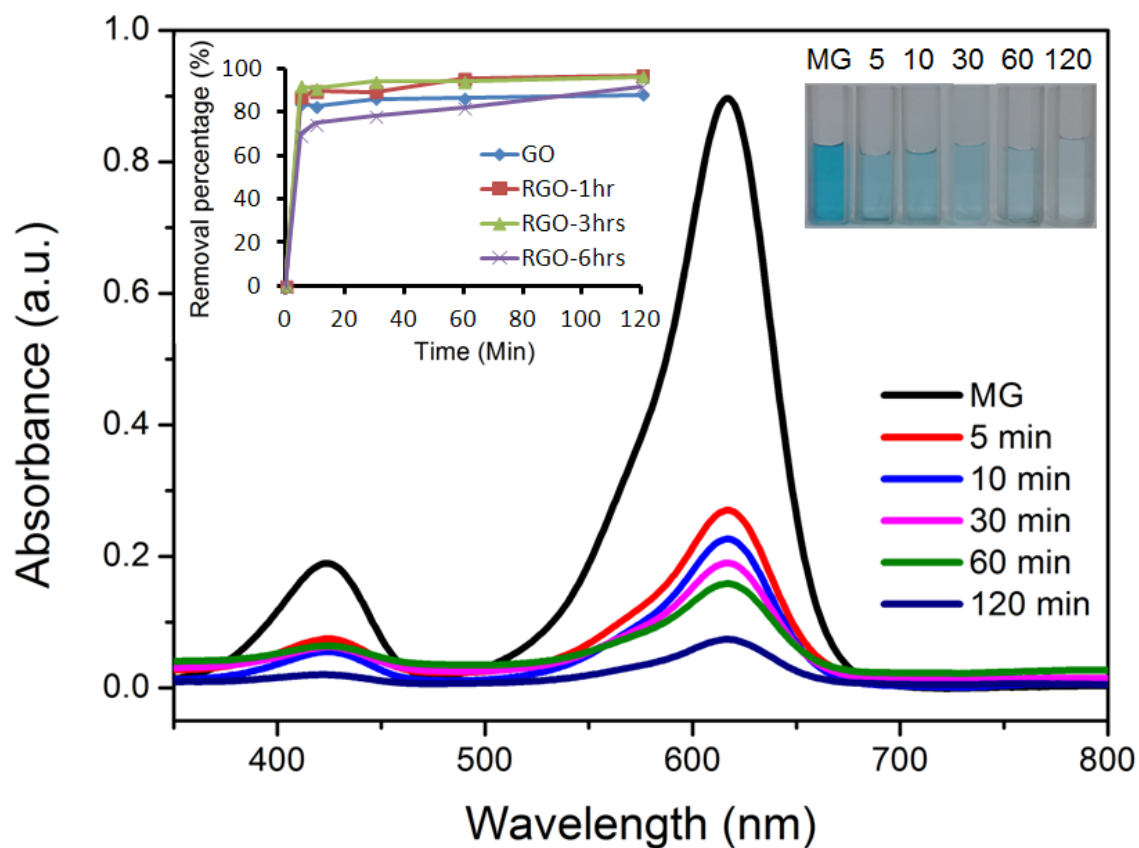


Figure 4 (a) XRD of Graphite, GO and RGO-6hrs (b) TEM image of RGO-6hrs sample



250  
 251 Figure 5 Removal of Malachite green dye using RGO-6hrs sample and graph showing change  
 252 in the removal percentage with time for GO, RGO-1hr, RGO-3hrs and RGO-6hrs samples  
 253 (Inset)